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# Synthesis of High Molar Mass Poly(alkylene phosphate)s by Polyaddition of Diepoxides to Difunctional Phosphoric Acids: Unusual Elimination of the Side Reactions

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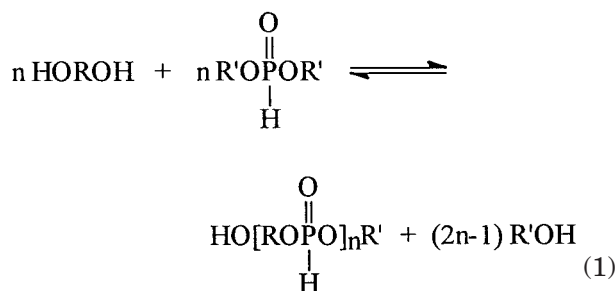
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**ABSTRACT:** The reaction between diepoxides and difunctional acids of phosphorus was studied as a potential route to linear polyesters of phosphoric acid. The reaction between diepoxide and P—OH groups in H<sub>3</sub>PO<sub>4</sub> and related acids leads to linear phosphates, but cyclic phosphates are also formed as side products. The formation of such unreactive groups terminates polyaddition. However, cyclization is practically eliminated when the epoxide ring is fused to another ring, such as in cyclohexene oxide. A commercially available diepoxide containing two cyclohexene oxide moieties, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ERL), was, therefore, used for polyaddition studies. Indeed, in the polyaddition of ERL with ethylphosphoric acid, high molecular weight (number-average molecular weight up to 10<sup>4</sup>) linear polyphosphates were obtained. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 3024–3033, 2001

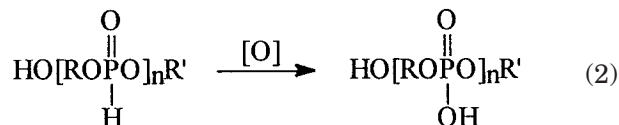
**Keywords:** addition polymerization; diepoxides; difunctional acid of phosphorus; poly(alkylene phosphate)s; heterogeneous polymers; kinetics (polym.)

## INTRODUCTION

In a series of previous articles, we described the synthesis of high molar mass poly(alkylene phosphate)s. The most general method is based on the polycondensation of diesters of H-phosphonic acid with diols<sup>1–3</sup> as shown:



Resulting linear poly(alkylene H-phosphonate)s are further oxidized to the corresponding poly(alkylene phosphoric acid)s:<sup>4</sup>

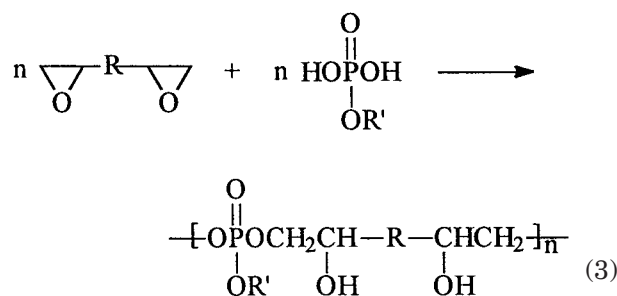


Methods based on the direct polymerization of cyclic esters of phosphoric acid or cyclic H-phosphonates were also elaborated.<sup>5,6</sup>

One can envision an alternative approach to the synthesis of high molar mass polyphosphates that is based on the polyaddition of difunctional acids of phosphorus to diepoxides as shown:

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HO— groups may be located at either the  $\alpha$ - or  $\beta$ -carbon atom, depending on the direction of ring opening.

Such a process could have some advantages over the earlier developed processes, including

- Milder reaction conditions.
- The possibility of a direct synthesis of polyphosphates (eliminating the oxidation step) with monoesters of phosphoric acids as reactants for the polyaddition process.

However, complications may arise because of possible side reactions resulting from

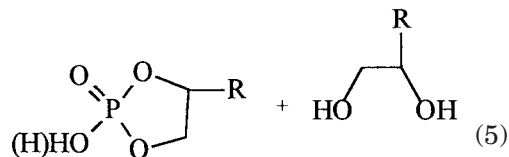
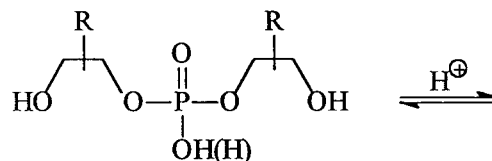
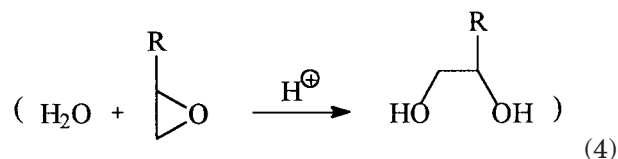
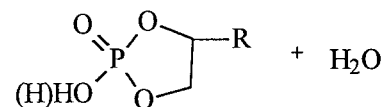
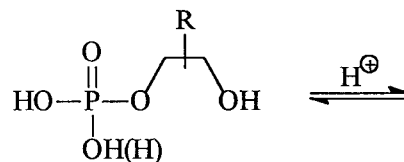
- The participation of the epoxide rings in reactions other than polyaddition to the P—OH group, such as in acid-catalyzed polymerization,
- The participation of C—OH groups formed as a result of epoxide ring opening in reaction with either another epoxide ring (in the presence of an acid) or a phosphate ester group (transesterification).

To estimate to what extent these reactions may compete with the addition of the epoxide groups to the P—OH groups, model reactions with simple monoepoxides and different P—OH acids were studied.<sup>7</sup> The addition of monofunctional P—OH acid, diethylphosphoric acid (DEPA; diester of phosphoric acid), to ethylene oxide proceeded at high conversions with reasonable rates, catalyzed by the P—OH groups themselves.<sup>8</sup>

The reaction of monofunctional P—OH acid with monosubstituted oxiranes led to a mixture of products resulting from two possible directions of ring opening. The fractions of products of  $\alpha$ - and  $\beta$ -ring opening depended on the nature of the substituent.<sup>9</sup>

In general, as a result of the opening of the epoxide ring, a hydroxyl group is formed, and it may participate in intramolecular transesterifica-

tion with the formation of cyclic phosphate groups. Indeed, the reaction of phosphoric or phosphorous acid with monosubstituted monoepoxides leads, in addition to linear products of addition, to cyclic phosphates as follows:



Cyclic phosphate groups, which can clearly be detected with <sup>31</sup>P NMR, constitute up to 10 mol % of the total phosphorus. Cyclic phosphate groups are stable under the conditions of the reaction. Therefore, reactions 4 and 5, from the point of view of potential polyaddition processes shown in reaction 3, correspond to termination, limiting further chain propagation. Cyclization processes are even more pronounced for derivatives of H-phosphonic acid, where up to 70 mol % of the cyclic structures (with respect to the total phosphorus in the polymer) have been observed.<sup>10</sup>

Therefore, to successfully apply the reactions shown in reaction 3 for the synthesis of high molar mass polyphosphates, we should eliminate the cyclization shown in reactions 4 and 5.

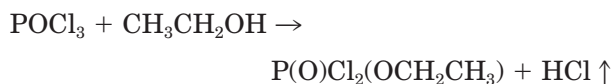
It may be argued that cyclization could be hampered by increased steric crowding around the C—OH group. Increasing the size of the substituent in monosubstituted epoxides apparently is not sufficient because from the two possible isomeric products of ring opening, one contains the primary hydroxyl group, and the substituent is located on carbon in the  $\beta$  position to the reacting C—OH group. Thus, at least for this regioisomer, the size of the substituent has little effect on steric crowding in the vicinity of the hydroxyl group. If, however, the oxirane ring is substituted at both carbon atoms, then independently of the direction of ring opening, only secondary hydroxyl groups will be present in the product, and in such a case, the presence of the substituent should affect the extent of intramolecular reaction.

In this article, we report the results of studies of the corresponding model systems and their extension to the real polyaddition processes involving diepoxides and difunctional P—OH acids, leading to the high molar mass poly(alkylene phosphate)s.

## EXPERIMENTAL

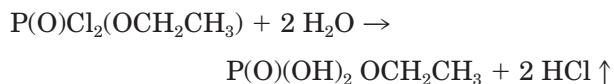
Cyclohexene oxide (CHO; 98% pure; Aldrich), *trans*-2,3-epoxybutane (TEB; 96% pure; Aldrich), and *cis*-2,3-epoxybutane (CEB; 97% pure; Aldrich) were dried over calcium hydride and distilled; fractions boiling at 129–130, 54–55, and 60–61 °C, respectively, were collected. 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ERL; purity not specified; Aldrich) was purified by vacuum distillation. The fraction boiling at 120 °C was collected. The purity according to GLC was greater than 98.5%.

Ethylphosphoric acid (EPA) was obtained via the following reactions:



$\text{POCl}_3$  (90 g, 0.59 mol) was dissolved in 40 mL of  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{CH}_2\text{OH}$  (27 g, 0.59 mol) dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise at 5 °C within 1 h.  $\text{CH}_2\text{Cl}_2$  was then removed on a rotary evaporator, and the remaining product was distilled. The fraction boiling at 68–70 °C and 23 mmHg was collected. Subsequent vacuum distillation with a 100-mm Vigreux column gave

40 g of the product with a purity greater than 99% according to GLC analysis:



$\text{P(O)Cl}_2(\text{OCH}_2\text{CH}_3)$  (40 g) was added dropwise (within 2 h) to 150 mL of distilled water close to 0 °C. The HCl that formed was removed continuously by the application of reduced pressure (with a water pump). Water was then removed on the rotary evaporator, and the remaining liquid was dried to a constant weight on a vacuum line. The purity according to GLC analysis was greater than 99%.

$^1\text{H}$  NMR analysis and titration with 0.1 N NaOH indicated that the concentration of protons in the analyzed samples of the product was equal within 0.1% to the concentration of protons in pure, dry acid. Therefore, we can conclude that the concentration of residual water did not exceed 2 mol %.

DEPA was obtained according to a procedure described elsewhere<sup>11</sup> by the oxidation of diethyl phosphite with potassium permanganate. The product was distilled twice; the fraction boiling at 101–102 °C and 0.04 mmHg was collected.

NMR spectra were recorded with a Bruker AC 200 spectrometer at 200 MHz for  $^1\text{H}$  spectra, 50.33 MHz for  $^{13}\text{C}$  spectra, and 81.01 MHz for  $^{31}\text{P}$  spectra.

Gel permeation chromatography analysis was performed with a ConstaMetric 4100 pump, a set of two 300 mm  $\times$  7.80 mm columns (Phenomenex 550 and 5500 Å), and an RI ReFractor Monitor IV detector.

GLC analysis was performed with a Hewlett-Packard HP 5890 apparatus with flame ionization detection.

## RESULTS AND DISCUSSION

### Model Reaction: Addition of $\alpha$ - and $\beta$ -Disubstituted Epoxides to Monofunctional P—OH Acid

#### TEB–DEPA System

The reaction between DEPA and TEB was carried out in a 1,4-dioxane solution (directly in an NMR tube), and both the kinetics of the reaction and the structure of the product were studied with the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra. Equivalent amounts of

both reactants (0.085 M concentrations) were used. The reaction was rather slow; the apparent second-order rate constant was  $6 \times 10^{-5} \text{ mol}^{-1} \text{ L s}^{-1}$ . An analysis of the  $^{31}\text{P}$  NMR spectra revealed that, although up to about 50% conversions of the reactants the concentration of cyclics was negligible and the only reaction products detected were linear esters (with chemical shifts between  $\delta = 1$  and 3 ppm in  $^{31}\text{P}$  NMR), at the later stages of the process, signals corresponding to five-member cyclic esters (with chemical shifts between  $\delta = 15$  and 17 ppm in  $^{31}\text{P}$  NMR) were clearly detectable. On the basis of integration, it could be estimated that their fraction reached 16.3 mol % of the total phosphorus at 90% conversions of both reactants.

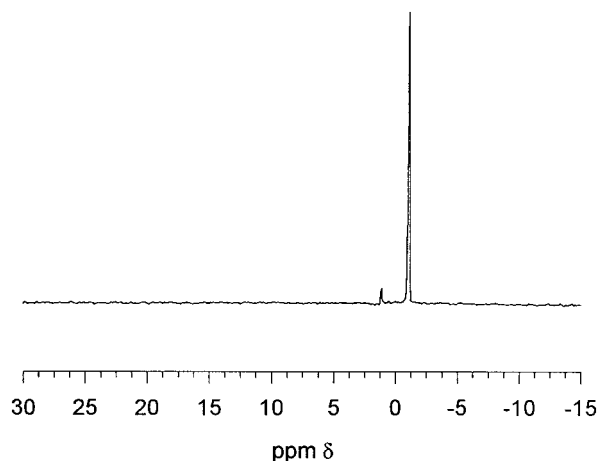
### CEB-DEPA System

The reaction between DEPA and CEB was studied in a way similar to that previously described. The apparent second-order rate constant was  $3.6 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ . An analysis of the  $^{31}\text{P}$  NMR spectra indicated that in this system initially the desired addition products were observed (chemical shifts between  $\delta = 0$  and 2 ppm); at the later stages, signals of cyclic phosphates appeared (chemical shifts between  $\delta = 15$  and 17 ppm); and their fraction increased to as much as about 60% of the total phosphorus at the final stage of the reaction.

Although the results obtained for DEPA-TEB and DEPA-CEB systems indicated that the presence of substituents at both the 2- and 3-positions of the epoxide ring was not sufficient to eliminate cyclization, they also showed that steric factors were indeed important because the extent of cyclization was very different for both isomers (60% for *cis*-isomer vs 16% for *trans*-isomer). Therefore, we decided to follow this line of thinking and introduce an additional steric restriction by using 2,3-disubstituted epoxide, in which both substituents were connected by an additional fused ring, CHO.

### CHO-DEPA System

The reaction between CHO and DEPA was studied in a 1,4-dioxane solution (directly in NMR tubes) at room temperature with  $^1\text{H}$  NMR. The range of reactant concentrations was 0.05–0.2 M. The apparent second-order rate constant was  $5.0 \pm 1.5 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$ . The addition of CHO to DEPA is, therefore, about  $10^2$  times faster than the addition of TEB to DEPA. Thus, compared with the high conversion of TEB, the high conver-



**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture containing CHO, DEPA, and 1,4-dioxane as a solvent at 25 °C.  $[\text{CHO}]_0 = 0.109 \text{ mol L}^{-1}$ ;  $[\text{DEPA}]_0 = 0.093 \text{ mol L}^{-1}$ ; reaction time = 1758 min.

sion of CHO may be reached in a considerably shorter time, leaving less time for transesterification to proceed. Indeed, an analysis of the  $^{31}\text{P}$  NMR spectra indicated that cyclic phosphates were virtually absent. Figure 1 shows the  $^{31}\text{P}$  NMR spectrum of the reaction mixture at the final stage of the reaction. Only signals of the linear triester ( $\delta = -0.75 \text{ ppm}$ ) and small signals corresponding to the unreacted DEPA ( $\delta = 1.40 \text{ ppm}$ ) were observed in the spectrum. There were no signals at chemical shifts around  $\delta = 15$ –17 ppm, characteristic of cyclic five-member phosphates.

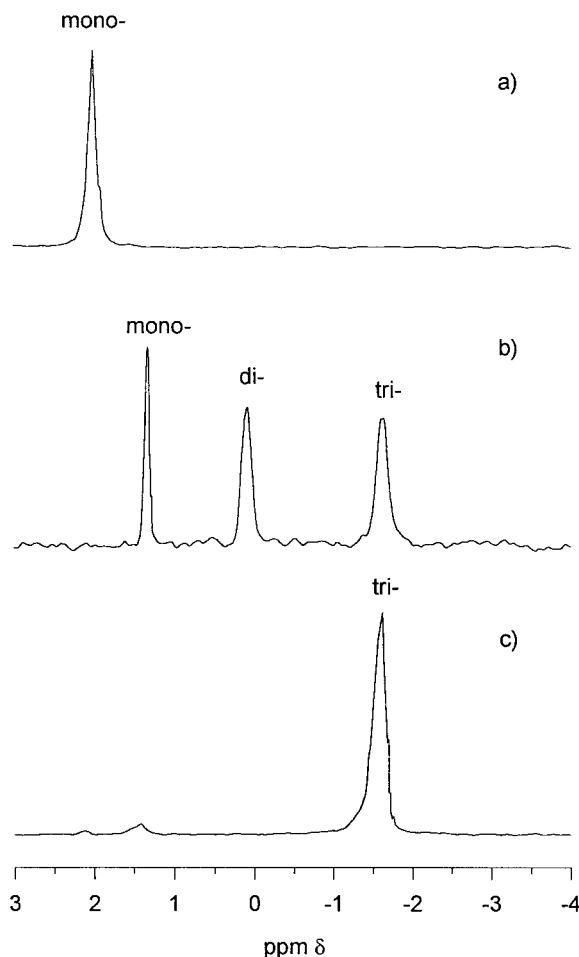
It may be concluded, therefore, that because of additional steric restriction related to the presence of a fused, relatively rigid ring in the CHO molecule, the intramolecular transesterification was eliminated and the reaction between CHO and DEPA led exclusively to linear phosphates.

### Polyaddition of ERL to EPA

ERL is a commercially available epoxy resin containing two CHO rings. Because model studies, described in the first part of this article, revealed that the addition of CHO to P—OH acids proceeds without the formation of cyclic phosphates, ERL was chosen as the difunctional epoxide offering the best chance to obtain high molar mass linear polyphosphate by its polyaddition with a difunctional P—OH acid, such as EPA.

The course of the reaction between ERL and EPA was followed by an analysis of  $^{31}\text{P}$  NMR





**Figure 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture (for the conditions, see Fig. 1) (a) at the start of the reaction, (b) in the course of the reaction at 63 mol % conversion of P—OH groups, and (c) at the end of the reaction at 96 mol % conversion of P—OH groups.

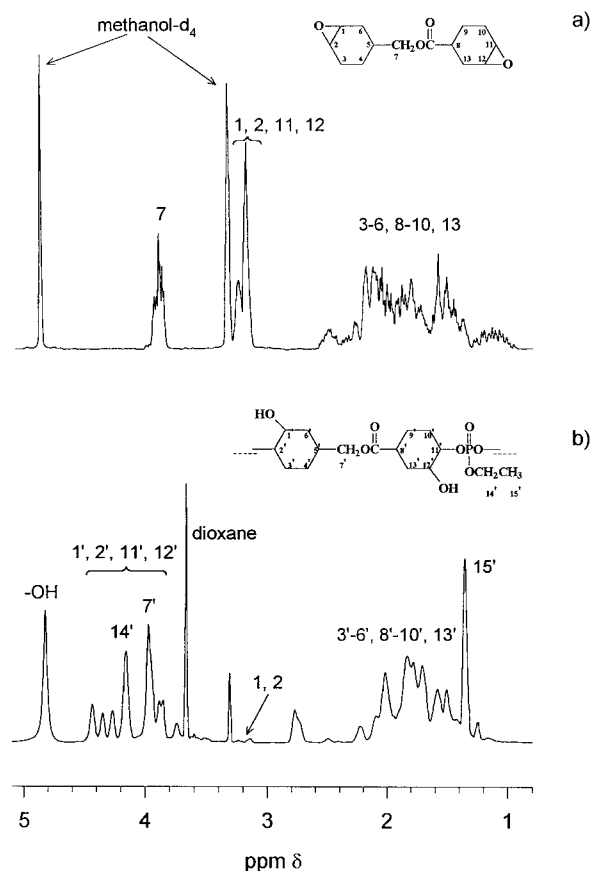
spectra (degree of conversion of EPA) and  $^1\text{H}$  NMR spectra (degree of conversion of ERL). Figure 2 shows the changes in the  $^{31}\text{P}$  NMR spectra of the reaction mixture in the course of the reaction. At time zero [Fig. 2(a)], only the signal of EPA (monoester) at about  $\delta = 2$  ppm is observed. In the course of the reaction, new signals appear, initially a signal at about  $\delta = 0$  ppm corresponding to diester (the product of the reaction of the first of the two P—OH groups in EPA) and then a signal at about  $\delta = -1.5$  ppm corresponding to triester (the product of the reaction of both P—OH groups of EPA). The spectrum of the reaction mixture at the stage when all three species are present in the system is shown in Figure 2(b). The spectrum shown in Figure 2(c) corresponds to the final stage of the reaction. More than 95 mol

% of the phosphorus is present in the form of triester (at ca.  $\delta = -1.5$  ppm), indicating a high conversion of P—OH groups. The other signal at about  $\delta = 1.5$  ppm (<5 mol % of the total phosphorus) appears in the region of absorption of phosphorus in EPA. This signal may, therefore, correspond to the unreacted EPA. Chemical shifts of monoesters and diesters change slightly in the course of the reaction because of the changing acidity of the medium.

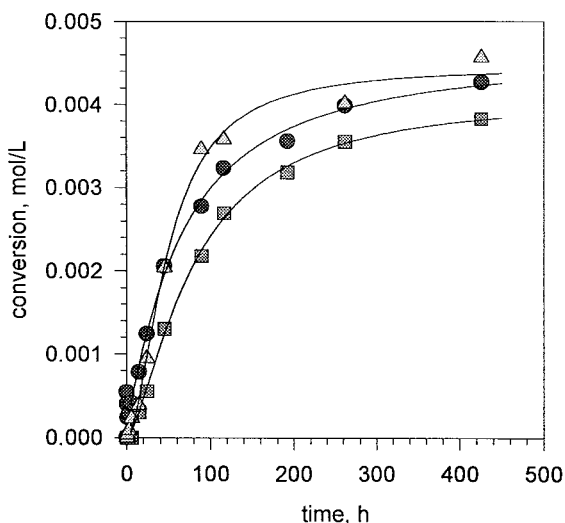
Spectra shown in Figure 2 indicate that the conversion of P—OH groups may be conveniently followed with  $^{31}\text{P}$  NMR.

Figure 3(a,b) shows  $^1\text{H}$  NMR spectra of ERL and the reaction mixture at the final stage of the reaction, respectively. Assignments of the signals are based on two-dimensional spectra (correlation  $^1\text{H}$ — $^{13}\text{C}$ ).

As shown in Figure 3(b), the characteristic changes of the spectra occur in the course of the reaction. The group of signals in the  $\delta = 3.10$ –



**Figure 3.**  $^1\text{H}$  NMR spectrum of (a) ERL in methanol- $d_4$  as a solvent and (b) the reaction mixture at the final reaction stage (for the conditions, see Fig. 1).



**Figure 4.** Conversion–time curves corresponding to the overall conversions of the P—OH groups and epoxy groups in the reaction between EPA and ERL at 25 °C with 1,4-dioxane as a solvent: ( $\blacktriangle$ ) conversion of P—OH groups (by  $^{31}\text{P}$  NMR), ( $\bullet$ ) conversion of epoxy groups (by  $^1\text{H}$  NMR), and ( $\blacksquare$ ) conversion of P—OH groups (by titration).  $[\text{EPA}]_0 = 0.00532 \text{ mol L}^{-1}$ ;  $[\text{ERL}]_0 = 0.00534 \text{ mol L}^{-1}$ .

3.25 ppm region, corresponding to the protons of the  $\text{>CH—O—}$  groups in epoxy rings, disappears, and a new group of signals in the  $\delta = 3.40\text{--}4.20$  ppm region, corresponding to the protons of the  $\text{>CH—O—P(O)<}$  and  $\text{>CH—OH}$  groups in open chain structures, appears in the spectrum. Although there is an overlap between the latter group of signals and the signal of the  $\text{—CH}_2\text{O—}$  groups, it is sufficient to follow the disappearance of the  $\delta = 3.10\text{--}3.25$  ppm signals, corresponding to CH groups in the epoxide ring, to determine the degree of conversion of the epoxide groups.

Thus, the conversion of epoxide groups can be easily followed with  $^1\text{H}$  NMR.

#### Kinetics of the Reaction between ERL and EPA

The kinetics of the reaction between ERL and EPA in a 1,4-dioxane solution was studied by the withdrawal of samples of the reaction mixture at preset time intervals, the termination of the reaction by titration of unreacted P—OH groups with 0.1 N NaOH, and the analysis of  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra of the neutralized reaction mixtures.

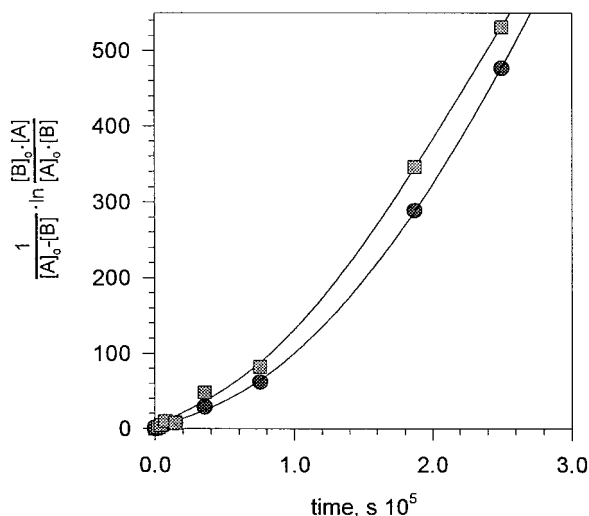
Figure 4 shows the conversion–time curves corresponding to the overall conversion of P—OH groups and epoxy groups. As shown in Figure 4,

there is a significant discrepancy between conversions of the P—OH groups determined by titration with 0.1 N NaOH to pH 12 and by  $^{31}\text{P}$  NMR. One possible reason for this discrepancy could be related to different relaxation times of the phosphorus nuclei in EPA (monoester), diester, and triester after neutralization of the P—OH groups with NaOH. To check this possibility, we recorded  $^{31}\text{P}$  NMR spectra of neutralized reaction mixtures containing different proportions of EPA, diester, and triester at different resonance-delay (RD) values (RD corresponds to the time span between subsequent pulses in seconds).

The results showed that the recorded signal intensities changed with changing RD, indicating that the response was not simply proportional to the concentration of related species. Moreover, the changes were different for different species; for example, the apparent intensity of a signal corresponding to triester decreased with increasing RD, whereas the opposite was true for the signal of EPA. To complicate the situation still further, the character of the changes depended on the composition of the reaction mixture. The dependence of the apparent signal intensity of a signal corresponding to the triester on RD was much more pronounced for the reaction mixture containing approximately 50 mol % triester than for the reaction mixture containing approximately 80 mol % triester. This means that in the spectra recorded at any RD, the ratio of the observed intensity of signals to the real concentration ratio changed with conversion.

The observed phenomena are apparently due to the fact that after neutralization the components of the reaction mixture are converted into differently charged species: EPA is converted into dianion, the diester is converted into monoanion, and the triester does not carry any charge. This may explain the different relaxation times of the phosphorus nuclei in related species and the different dependencies of the apparent signal intensities on RD. At any composition of the reaction mixture, the dependence of the signal intensity on RD reached a plateau at an RD value close to 15 s. All the spectra were, therefore, recorded at RD = 15 s. Nevertheless, the results of  $^{31}\text{P}$  NMR analysis may involve some error, so an analysis of the kinetics of the reaction was based on conversions of P—OH groups determined by titration.

In the simplest case, the kinetics of the reaction between EPA and ERL may be analyzed on the assumption that the reactivity of the P—OH and epoxy groups in difunctional reactants does



**Figure 5.** Second-order kinetic plots for the reaction between ERL and EPA at 25 °C with 1,4-dioxane as a solvent: (■) rate of consumption of the P—OH groups by titration and rate of consumption of epoxy groups taken as equal to the rate of consumption of P—OH groups and (●) rate of consumption of the P—OH groups by  $^{31}\text{P}$  NMR and rate of consumption of the epoxy groups taken as equal to the rate of consumption of the P—OH groups.  $[\text{EPA}]_0 = 0.0105 \text{ mol L}^{-1}$ ;  $[\text{ERL}]_0 = 0.00557 \text{ mol L}^{-1}$ .

not depend on the position of the epoxy group (although the two are not equivalent) and on whether another group in the same molecule has already reacted; that is, the reactivity of the P—OH groups in the monoester is the same as in the diester, and the same is true for the reactivity of epoxy groups. Those are rather crude approximations, but the kinetic analysis was started this way to reveal how significant the deviations are from such a simple scheme. With these assumptions, the kinetics of the process is described by a second-order kinetic equation:

$$1/([B]_0 - [A]_0) \cdot \ln([A]_0[B]_t/[B]_0[A]_t) = kt \quad (6)$$

where  $[A]$  and  $[B]$  denote the concentrations of both reactants ( $B$  denotes the one used in excess).

A typical plot according to eq 6 is shown in Figure 5. As indicated earlier, the plots based on the concentrations of the P—OH groups determined either from  $^{31}\text{P}$  NMR analysis or titration differ to some extent. What is more important is that the plots are not linear, showing significant upward curvature. Thus, the kinetics of the reaction cannot be described by a single rate constant. A rough approximation can be obtained if we

measure the slope of the curve at the early and late stages of the reaction. Such an estimate gives  $k = 7.5 \times 10^{-1} \text{ mol}^{-1} \text{ L s}^{-1}$  for the apparent rate constant at the early stage and  $k = 30 \times 10^{-1} \text{ mol}^{-1} \text{ L s}^{-1}$  for the apparent rate constant at the late stage of the reaction. This difference may indicate that the reactivity of the second group in ERL or EPA (or both) is higher than the reactivity of the first group.

To confirm this conclusion, we analyzed the kinetics of the reaction not only on the basis of the overall consumption of the reacting groups as described previously but also on the basis of the consumption of individual species in terms of the scheme corresponding to the set of two consecutive reactions.

#### *Analysis of the Kinetics of the Reaction in Terms of a Scheme Involving Two Second-Order Consecutive Reactions*

The  $^{31}\text{P}$  NMR spectra allow the determination of not only the overall rate of P—OH group consumption but also the changes of the EPA, diester, and triester concentrations in the course of the reaction. Therefore, a more detailed approach for analyzing the kinetics of the reaction is possible. The process may be treated as a series of consecutive reactions. In the first one, EPA is converted into the diester; in the second one, the diester is converted into the triester.

The same is true for the second component. Diepoxide is converted in the first step into the monoepoxide (the second group being the phosphate ester group), and in the second step, this species is converted into diester. An analysis of  $^1\text{H}$  NMR spectra does not, however, allow an independent observation of the epoxy groups in diepoxide and monoepoxide, and only the overall concentration of epoxy groups can be determined from the spectra.

Thus, this approach may be used only to analyze the kinetics on the basis of changes of concentration of the phosphoric acid esters (monoester, EPA; diester, the product of the reaction of one P—OH group in EPA; and triester, the product of the reaction of both P—OH groups in EPA) because signals corresponding to the three involved species may be separately observed and quantitatively analyzed in  $^{31}\text{P}$  NMR spectra.

The kinetic equations for the set of two first-order (or pseudo-first-order) consecutive reactions can easily be solved. The studied reaction is, however, at least second-order (first-order with re-



spect to P—OH groups and first-order with respect to epoxy groups). Such a scheme can be solved by numerical integration (curve fitting) of the following set of kinetic equations:

$$d[\text{EPA}]/dt = -k_1[\text{EPA}][\text{epoxy groups}]$$

$$d[\text{diester}]/dt = k_1[\text{EPA}][\text{epoxy groups}] - k_2[\text{diester}][\text{epoxy groups}]$$

$$d[\text{triester}]/dt = k_2[\text{diester}][\text{epoxy groups}]$$

$$d[\text{ERL}]/dt = -k_1[\text{EPA}][\text{epoxy groups}] - k_2[\text{diester}][\text{epoxy groups}]$$

An analysis of the experimental data for the reaction performed in a 1,4-dioxane solution at equal initial concentrations of both reactants ( $[\text{EPA}]_0 = [\text{ERL}]_0 = 5.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) gives the best fit for the following values of the rate constants:

$$k_1 = 4.4 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} \text{ (1,4-dioxane, 25 } ^\circ\text{C)}$$

$$k_2 = 8.1 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} \text{ (1,4-dioxane, 25 } ^\circ\text{C)}$$

In Figure 6, calculated plots are compared with experimental points. When, however, the same approach was used to analyze the kinetics of the reaction performed at a twofold excess of P—OH groups ( $[\text{ERL}]_0 = 5.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ,  $[\text{EPA}]_0 = 10.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ), values of the rate constants about 2 times higher were obtained:

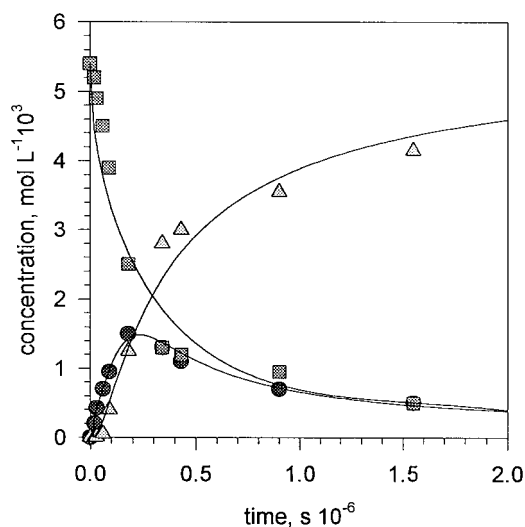
$$k_1 = 8.0 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} \text{ (1,4-dioxane, 25 } ^\circ\text{C)}$$

$$k_2 = 15.0 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} \text{ (1,4-dioxane, 25 } ^\circ\text{C)}$$

In both sets of results,  $k_2$  is approximately 2 times higher than  $k_1$ .

The kinetic results may be summarized as follows:

1. An analysis of the time–conversion curves indicates that the rates of consumption of both reacting groups, that is, P—OH groups and epoxy groups, are the same. This indicates that none of these groups is consumed in a reaction other than addition.
2. The full kinetic scheme of the reaction between ERL and EPA involves, in fact, several consecutive reactions that may pro-



**Figure 6.** Experimental (points) and calculated (lines) changes in the concentrations of (■) monoester (EPA), (●) diester, and (▲) triester in the course of the reaction with ERL at 25 °C with 1,4-dioxane as a solvent. The calculated curves correspond to  $k_1 = 4.4 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$  and  $k_2 = 8.1 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ .  $[\text{EPA}]_0 = 0.00532 \text{ mol L}^{-1}$ ;  $[\text{ERL}]_0 = 0.00534 \text{ mol L}^{-1}$ .

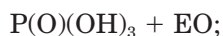
ceed with the same or different rate constants. In both difunctional components of the reaction mixture, the first group may react with a different rate constant than the second one. Indeed, an analysis of the kinetics in terms of the second-order consecutive reactions indicates that the second rate constant is approximately 2 times higher than the first one.

The applied analytical methods allow the determination of the concentrations of the products of the first and second reactions only for one of the two reactants. Therefore, the analysis was based on the changes in the concentrations of  $\text{ROP}(\text{O})(\text{OH})_2$  (i.e., EPA),  $(\text{RO})_2\text{P}(\text{O})\text{OH}$  (i.e., diester), and  $(\text{RO})_3\text{PO}$  (i.e., triester). Thus, the values of the rate constants were derived under the assumption of different reactivities of P—OH groups in EPA and diester. Similar results could, however, be obtained if the reactivity of P—OH groups in both species were the same but the reactivity of the remaining epoxy group in monoepoxide was higher than that of any of two epoxy group in diepoxide. This is, however, much less likely. The exact dependence of concentrations of  $\text{ROP}(\text{O})(\text{OH})_2$  (i.e., EPA),  $(\text{RO})_2\text{P}(\text{O})\text{OH}$  (i.e., diester), and  $(\text{RO})_3\text{PO}$  (i.e., triester) on time should

be different in both instances, but if the differences were not large, both cases could be indistinguishable, if we consider the limited accuracy of the measurements.

Thus, these results indicate instead that diester formed in the first step was more reactive than the starting compound (monoester).

As mentioned previously, the differences in reactivity between two subsequently reacting groups occurs in phosphoric acid derivatives rather than in epoxy compounds. Two epoxide rings in ERL are separated by several atoms, so the change in the nature of the bond with the reaction of one epoxide group should not affect significantly the reactivity of other group. However, replacing the acidic HO- group connected to phosphorus by the RO- ester group may considerably affect the reactivity of the other P—OH group connected to the same phosphorus atom. Such an effect was indeed observed in the model system earlier, when the addition of monoepoxides to phosphoric acid was studied.<sup>8</sup> The reactivity of the P—OH groups increased with an increasing degree of esterification. The rate constants measured for the addition of ethylene oxide to phosphoric acid and its derivatives were as follows:



$$k = 2.4 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} (1,4\text{-dioxane, } 25^\circ \text{C})$$

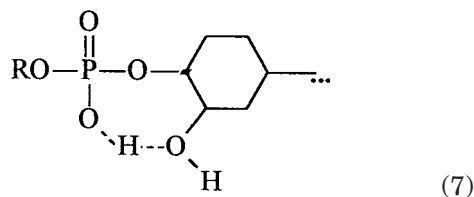


$$k = 4.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} (1,4\text{-dioxane, } 25^\circ \text{C})$$



$$k = 9.7 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1} (1,4\text{-dioxane, } 25^\circ \text{C})$$

The observed effect was related to the hydrogen bonding between the remaining P—OH group and C—OH group formed with the reaction of the P—OH group with an epoxide ring. The same explanation may be valid for this studied system:



Both rate constants (more correctly, rate coefficients),  $k_1$  and  $k_2$ , apparently depend on the concentration of EPA being higher at higher  $[\text{EPA}]_0$ .

This indicates that an external order with respect to EPA (i.e., P—OH groups) may be higher than one. Although on the basis of the available data the reaction order cannot be determined with any reliability, the fact that the apparent rate constant (calculated on the assumption that the reaction is first-order with respect to both reactants) increases twice with a twofold increase in the P—OH concentration may indicate that the reaction is second-order with respect to P—OH groups:

$$R = k[\text{P—OH}][\text{epoxy groups}]$$

However, if  $k = k'[\text{P—OH}]$ , then

$$R = k'[\text{P—OH}]^2[\text{epoxy group}]$$

Such dependence would indicate that in the reaction of the P—OH group with an epoxy group, an additional P—OH group participates in the elementary step; that is, the reaction is catalyzed by P—OH groups. This would be analogous to an uncatalyzed esterification reaction between carboxyl and hydroxyl groups, which, although involving one carboxyl group and one hydroxyl group, is known to be kinetically of the second order with respect to the carboxyl group because an additional carboxyl group participates in the reaction as a catalyst.

The observation that the apparent rate constant is considerably higher for the second reacting P—OH group has important practical implications. The increasing reactivity provides to some extent compensation for the decreasing rate of the reaction due to the decreasing concentration of reacting groups, allowing the polyaddition reaction to be carried out up to high conversions with reasonable rates.

### Synthesis of High Molecular Weight Polyphosphates via the Polyaddition of ERL to EPA

The synthesis of poly(alkylene phosphate)s by the polyaddition of ERL to EPA was carried out in 1,4-dioxane as a solvent. Kinetic experiments indicated that neither of the reactants underwent any side reactions under the conditions used (diluted solutions). In experiments aimed at the synthesis of polymers, more concentrated solutions were used. To eliminate the possibility of side reactions involving epoxide groups, we slowly added a solution of diepoxide in 1,4-dioxane to a solution of EPA in 1,4-dioxane to keep a low instantaneous concentration of epoxy groups in the system.

The conversion of P—OH groups and the progress of the reaction were followed by the recording of  $^{31}\text{P}$  NMR spectra of the reaction mixture. At about 50% of the overall conversion of the P—OH groups, a homogeneous solution separated into two liquid phases, a high-viscosity lower phase and a lower viscosity upper phase. A  $^{31}\text{P}$  NMR analysis of both phases showed that the complete conversion of the P—OH group (no signal could be detected in the  $^{31}\text{P}$  NMR spectra) was reached after the addition of an amount of the diepoxide corresponding to a molar ratio of the epoxy group concentration to the P—OH group concentration equal to 1.004. Thus, the reaction proceeded with a nearly perfect 1:1 stoichiometry.

The products from both phases were isolated separately through the evaporation of the solvent. From the high-viscosity phase, 72 mol % of the product with a number-average molecular weight ( $M_n$ ) of 11,600 [vapor phase polyaddition (vpo) in 1,4-dioxane] was obtained, whereas from the low-viscosity phase, 28 mol % of the product with an  $M_n$  value of 9800 (by the same method) was recovered. The  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra of the products isolated from both phases were identical.

Products isolated from both high-viscosity and low-viscosity phases were practically identical, so we concluded that the separation of the originally homogeneous solution into two phases was due to the limited solubility of the polymer in 1,4-dioxane. When a certain critical concentration was reached, phase separation occurred, leading to a polymer-rich phase (a polymer containing some solvent and thus forming a high-viscosity but still liquid phase) and a solvent-rich phase (i.e., a diluted solution of polymer in 1,4-dioxane).

In  $^{31}\text{P}$  NMR spectra of the combined products, only the signal of phosphorus in the triester group (linear chain unit) could be detected. No signals were observed in the  $\delta = 15\text{--}17$  ppm region, indicating that cyclic phosphate units were absent. Signals of phosphorus in monoester (at  $\delta = 2$  ppm) and diester (at  $\delta = 0$  ppm) were not detectable. This indicates that EPA (monoester) was consumed quantitatively and that either there were no phosphate end groups (diesters) or their content was too low to be detected by  $^{31}\text{P}$  NMR. If all macromolecules with an  $M_n$  value close to  $10^4$  were terminated with phosphate end groups, their contents should be equal to 3 mol % of the total phosphorus.

These results indicate that the polyaddition of ERL to DEPA leads to relatively high molar mass linear poly(alkylene phosphate)s.

## CONCLUSION

The results presented in this article indicate that the polyaddition of ERL to DEPA leads to relatively high molar mass linear poly(alkylene phosphate)s with  $M_n$  values up to  $10^4$ . Thus, C—OH groups formed by the opening of the epoxide ring do not participate in a reaction with a terminal phosphate group because such a reaction would terminate polyaddition through the formation of an unreactive cyclic phosphate group and preclude the formation of the higher molecular weight polymer. Although this side reaction was observed for a number of different epoxy compounds, it was absent for derivatives of CHO; this might have been related to the unfavorable steric position of the C—OH group with respect to the phosphate group when both were connected to the cyclohexane ring. The application of diepoxides containing two CHO moieties to polyaddition with difunctional acids of phosphorus provides, therefore, an interesting alternative to the known methods of synthesizing high molecular weight linear polyphosphates.

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